# A Comprehensive Assessment of the Accuracy of Ideal Adsorbed Solution Theory for Predicting Binary Adsorption of Gas Mixtures in Porous Materials

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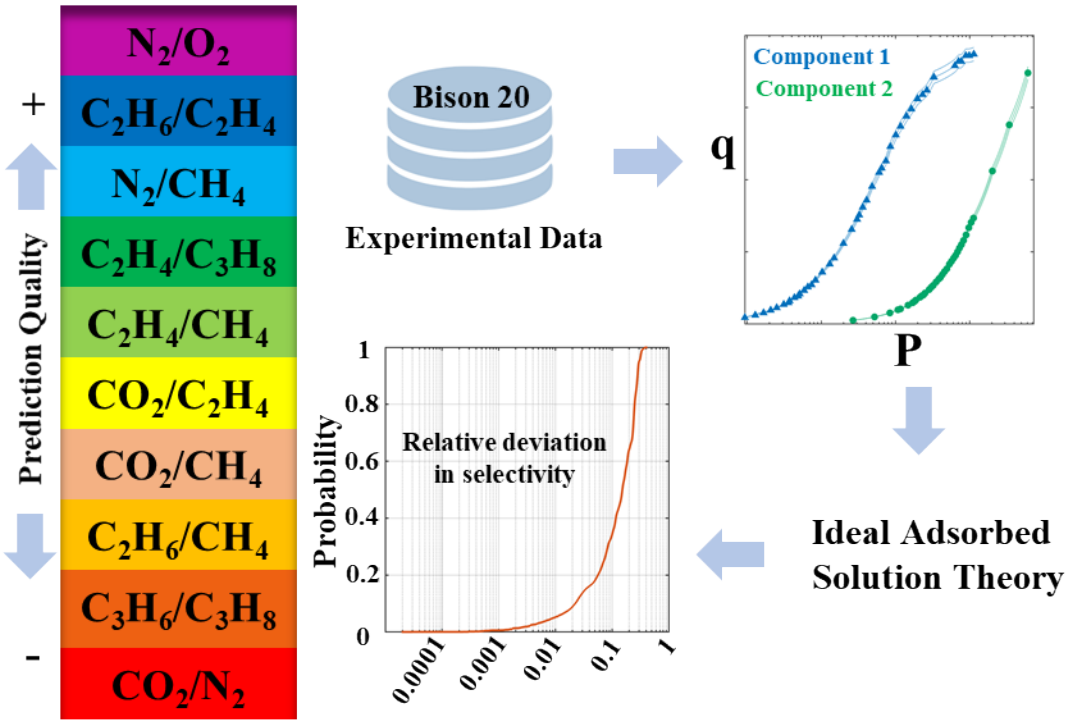
**TOC graphic**


N2/O2
C2H6/C2H4
N2/CH4
C2H4/C3H8
C2H4/CH4
CO2/C2H4
CO2/CH4
C2H6/CH4
C3H6/C3H8
CO2/N2
+
-
Prediction Quality
Bison 20
Experimental Data
Component 1
Component 2
q
P
Ideal Adsorbed
Solution Theory
Relative deviation
in selectivity
Probability
1
0.8
0.6
0.4
0.2
0
0.0001
0.001
0.01
0.1
1

**Abstract**

Quantifying the adsorption of chemical mixtures in porous adsorbents is critical to developing these materials for useful separations applications. Ideal Adsorbed Solution Theory (IAST) is the most widely applied mixing theory for predicting mixture adsorption using single-component adsorption data, but a perceived lack of experimental data has limited previous efforts to explore the accuracy of IAST in a systematic way. In this paper we take advantage of a large collection of binary experimental data for gas adsorption that became available recently (X. Cai et al., Ind. Eng. Chem. Res., 60 (2021) 639) to tackle this issue. We identify more than 400 examples in which binary adsorption data and single component data are available in the same publication, and apply IAST to all of these examples. This analysis includes experimental data from 63 gas mixtures of 37 different molecular species and 174 different adsorbents. In addition to being the most systematic evaluation to date of the accuracy of IAST for gas adsorption, this data will be valuable for future efforts to test or develop mixing theories that improve upon IAST.

## I. Introduction

Adsorption-based separations are one example of the methods that could lead to dramatic reductions in energy use in performing chemical separations[1]. A fundamental requirement for developing an adsorption-based separation is knowledge of the adsorption isotherms of the species of interest for one or more potential adsorbents[2]. Although direct information on the adsorption of chemical mixtures is the primary quantity of interest for these isotherms, the challenges of making measurements with adsorbed mixtures and the sheer number of mixtures that exists[3] means that information must often be deduced from single-component data using approximate mixing theories.

The most widely used mixing theory for predicting mixture adsorption is Ideal Adsorbed Solution Theory (IAST), introduced by Myers and Prausnitz over 50 years ago[4, 5]. A key question for use of IAST (or any of the improved mixing theories that have been proposed[6-8]) is how accurate it is for various physical examples or regimes of interest. One useful approach to this question is to use data from molecular simulations, since in these simulations obtaining mixture adsorption data is straightforward and issues associated with numerical uncertainties at low or high pressures can be avoided[9]. Recent examples of testing the performance of IAST with molecular simulations include simulations of $CO_2/CH_4$ mixtures in a large collection of structurally disordered porous materials and efforts to use IAST in conjunction with machine learning to predict the adsorption of diverse mixtures[10, 11].

A challenge with testing the accuracy of IAST and similar mixing theories with data from molecular simulations is that the models used in these simulations are idealized in a number of ways. Almost all molecular simulations of adsorption focus on crystalline porous materials that do not include the various defects and imperfections that are ubiquitous in real materials. These simulations also typically rely on approximate force fields to describe adsorbate-adsorbent interactions[12]. For these reasons, it would be very useful to systematically test the accuracy of mixing theories for adsorption using experimental data.

An obvious challenge with comparing IAST to experimental data is obtaining suitable data for this purpose[13]. Until recently, collections of mixture adsorption data for gas adsorption in porous

materials that had been compiled contained only a limited number of examples [6, 14, 15]. A recent systematic literature analysis, however, collected a much larger number of experimental studies than anticipated and put this data in a publicly accessible format known as the BISON-20 data set[16]. In this paper, we make a comprehensive comparison between data available from the BISON-20 data set and predictions from IAST. We restrict our attention to examples in which the mixture adsorption data and the necessary single-component adsorption data are available from the same set of published experiments. This approach reduces uncertainty about variations among materials or other factors between different published studies[17]. This allows us to examine more than 400 distinct sets of experiments for gas mixtures in porous materials, making this work by far the most comprehensive comparison between IAST and experimental mixture adsorption data to date.

It is tempting when thinking about the accuracy of IAST to ask whether the theory "works". This description, however, is too simplistic because the level of accuracy that is desirable is likely to depend strongly on context. In efforts to screen enormous numbers of adsorbents or mixtures, for example, relatively low levels of accuracy might be acceptable because these activities should be combined with more detailed calculations or experiments for the materials thought to be the most promising. In contrast, detailed process optimization of a specific separation with a known adsorbent would require highly accurate descriptions of mixture adsorption. For this reason, throughout our discussion below we analyze the agreement (or lack of agreement) between IAST and experimental data in terms of a range of thresholds rather than attempting to suggest a single criterion that delineates when IAST is accurate and when it is not.

## II. Materials and Methods

### Data Source

Experimental binary adsorption equilibrium data were retrieved from the BISON-20 data set[16]. This data set is the largest available collection of experimental mixture adsorption data, and includes data from over 900 binary gas mixture adsorption experiments including 125 different gas mixtures and 333 different adsorbents[16]. Besides the data, BISON-20 reports the source publication and also the type of adsorption experiment for each isotherm (e. g. absolute or excess). This facilitates checking the original publications to manually obtain further details of the

experiments. We inspected each experiment reported in BISON-20 by looking at the original publications to find the sources that also reported single-component isotherms. This led to a list of 589 experiments in which binary mixture results and the single-component adsorption isotherms for both adsorbing species was reported in the same publication (see Table S1). Our examination of the BISON-20 data revealed a small number of errors in the original BISON-20 collection due to, for example, placing data in wrong columns and labeling data with incorrect components. A detailed list of corrections associated with these issues is given in section S.2 in SI document. We strongly recommend that these corrections be applied to any future applications of the BISON-20 data.

Table S2 shows a wide range of units that is used to report adsorption data in the literature. We restricted our attention to adsorption data in which temperature, pressure, and loadings are either reported in or that could be converted to K, bar, and mol/kg units, respectively. In terms of gas/adsorbed phase compositions, we only considered the data reported in or that could be converted to mol/volume fraction. We also excluded from further consideration experiments reporting excess adsorption data and those reporting less than 4 state points per single-component isotherms. This process gave us a collection of 424 adsorption experiments covering 63 gas mixtures of 37 different molecular species and 174 different adsorbents (see Table S4). The gas composition for 35 (out of 424) binary mixture systems was been reported in volume fractions. We used the Lee-Kesler equation of state to convert these examples into mole fractions (see SI for more details).[18]

In instances where the diffusion of one or more adsorbed species is slow obtaining adsorption data that is fully equilibrated can be challenging. In some cases, this challenge may be more pronounced with adsorbed mixtures than with single component adsorption. Throughout our analysis we assumed that all of the single component and mixture data from BISON-20 is fully equilibrated.

**IAST calculations**

Although IAST has been widely used for the prediction of binary mixture adsorption[4, 5], a comprehensive assessment of its quality in describing the adsorption of gas mixtures in different adsorbents using experimental data has not previously been possible. The large collection of data described above makes this assessment feasible for the first time. An important aspect of

considering the accuracy of IAST predictions based on experimental data is the impact of uncertainty in the underlying data. Quantitative estimates of experimental uncertainties are only available in a small fraction of the experimental reports that provided the data we used.[19-24] Several estimates of uncertainty have been reported for experimental single-component adsorption data. Sudibandriyo et al.[19] studied adsorption of $CH_4$, $N_2$, and $CO_2$ in an activated carbon using volumetric and gravimetric methods. By comparing the two methods, they reported 1.8-6.4% uncertainty for the data. Another example has provided by Shirani and Eic[20], who measured adsorption of $CO_2$, CO, and $C_2H_4$ in zeolite NaY using differential column and gravimetric techniques. They found their differential column data are, respectively, in average, 4.7 - 6.1% uncertain compared with the corresponding gravimetric data. Hoffman et al.[25] and later Avijegon et al.[22] discussed a detailed method to calculate the uncertainty of adsorption data measured by dynamic column breakthrough techniques. They concluded that well controlled experiments had uncertainties of at least 2.4%. Taking these examples into account, we chose ±2.5% as the uncertainty estimate for all of the single-component data used below. This value was deliberately chosen in a conservative way that is likely to underestimate the uncertainty in many cases, since this value can go up to ±30% in some cases depending on the type of experiment.[21]

We assumed the uncertainty is normally distributed around the loadings of every single-component adsorption state point as well as loadings from data for binary mixtures. For each single-component system we generated 11 independent isotherms in which the values for each loading were randomly sampled from this normal distribution. By performing IAST with all possible combinations of these single-component isotherms we were able to estimate the impact of uncertainty in the single-component data on predictions from IAST. For each binary system we interpolated all the corresponding uncertain single-component adsorption data sets and we used the pyIAST software[26] to perform IAST calculations for each of 121 combinations of the single-component isotherms that incorporated uncertainty. We applied this approach to all 424 of the binary systems listed in Table S3. pyIAST failed to complete IAST calculations for 13 systems for which the highest pressures available for the single-component adsorption data are much less than that the IAST requires (Table S5). We excluded these 13 systems from further analysis, meaning that we report results below from 411 systems.

IAST predicts the adsorbed loadings of each component in a binary mixture, $q_1^{ads}$, and $q_2^{ads}$ and the corresponding selectivity $S_{1/2}^{ads}$ using gas phase mole fractions, $y_1$ and $y_2$ as

$$S_{1/2}^{ads} = \frac{q_1^{ads}/q_2^{ads}}{y_1/y_2} \quad (1)$$

The quality of predictions with IAST depend not only on the uncertainty of the single-component isotherms but also on the pressure range over which these isotherms are available. The pyIAST package generates an "extrapolation" warning when applying IAST requires extrapolation of single-component adsorption data beyond the highest available pressure. In these cases, it is important to consider how data in this range is extrapolated; we return to this point below. Throughout the results below we distinguished between IAST predictions that required extrapolation and those that did not.

## III. Results and Discussion

Before discussing the application of IAST to a diverse collection of materials, we first illustrate our calculations using data for 1,4-dioxane/butan-2-one in FAU Y zeolite at 298 K[27]. We generated a distribution of 11 uncertain single-component isotherms for each component using uncertainties of ±2.5% as described above. The original single component isotherms for this example as well as the upper/lower bound uncertain isotherms are shown in Figure 1(a). For each of the 57 individual binary adsorption state points we performed IAST calculations using each of the 121 combinations of single component isotherms. For this example, this gives 57×121=6,897 independent predictions.

Figure 1(b) shows the adsorption loadings of mixtures of 1,4-dioxane and butan-2-one in FAU Y zeolite at 298 K from direct experiments with the binary mixtures and as predicted with IAST.[27] The uncertainties on the IAST results are derived from the 121 independent calculations for each state point described above. Perhaps surprisingly given the complexity of the adsorbing species the IAST predictions are in good agreement with the mixture experiments in many cases. We defined the relative deviation for each state point as the absolute difference between the experimental data and IAST results divided by the experimental data. Figure 1(c) shows a cumulative plot of the relative deviations for each component. IAST predicts the loadings of 1,4-

dioxane and butan-2-one with a relative deviation <50% in 81.7% and 99.5% of the available cases, respectively. Figure 1(d) shows a similar cumulative plot of the relative deviation for the adsorption selectivity. IAST predicts the selectivity with relative deviation <50% for 99.6% of the state points. If this relative deviation criterion is reduced to deviations <10%, Fig. 1(d) shows that 30.7% of the selectivity predictions meet this standard. We reiterate that the number of state points in this analysis is much larger than the number of points in the original experimental data because of the way we have included uncertainty in the data.

As shown in Table S6, IAST requires the single-component isotherms of 1,4-dioxane and butan-2-one in FAU Y zeolite at 298 K up to 0.0048 and 0.0082 bar, respectively, to apply to the full set of binary adsorption experiments. Although single-component data is available for butan-2-one up to 0.0089 bar, similar data are reported for 1,4-dioxane only up to 0.0025 bar. This means that our IAST calculations involve extrapolation beyond the single-component data for 7% of the binary state points. These predictions are shown in Figure 1(a) with a circle. The fraction of cases in which IAST predicts the selectivity of FAU Y zeolite for 1,4-dioxane over butan-2-one at 298 K with a relative deviation <50% is 94.2% in situations when extrapolated single-component data are used.

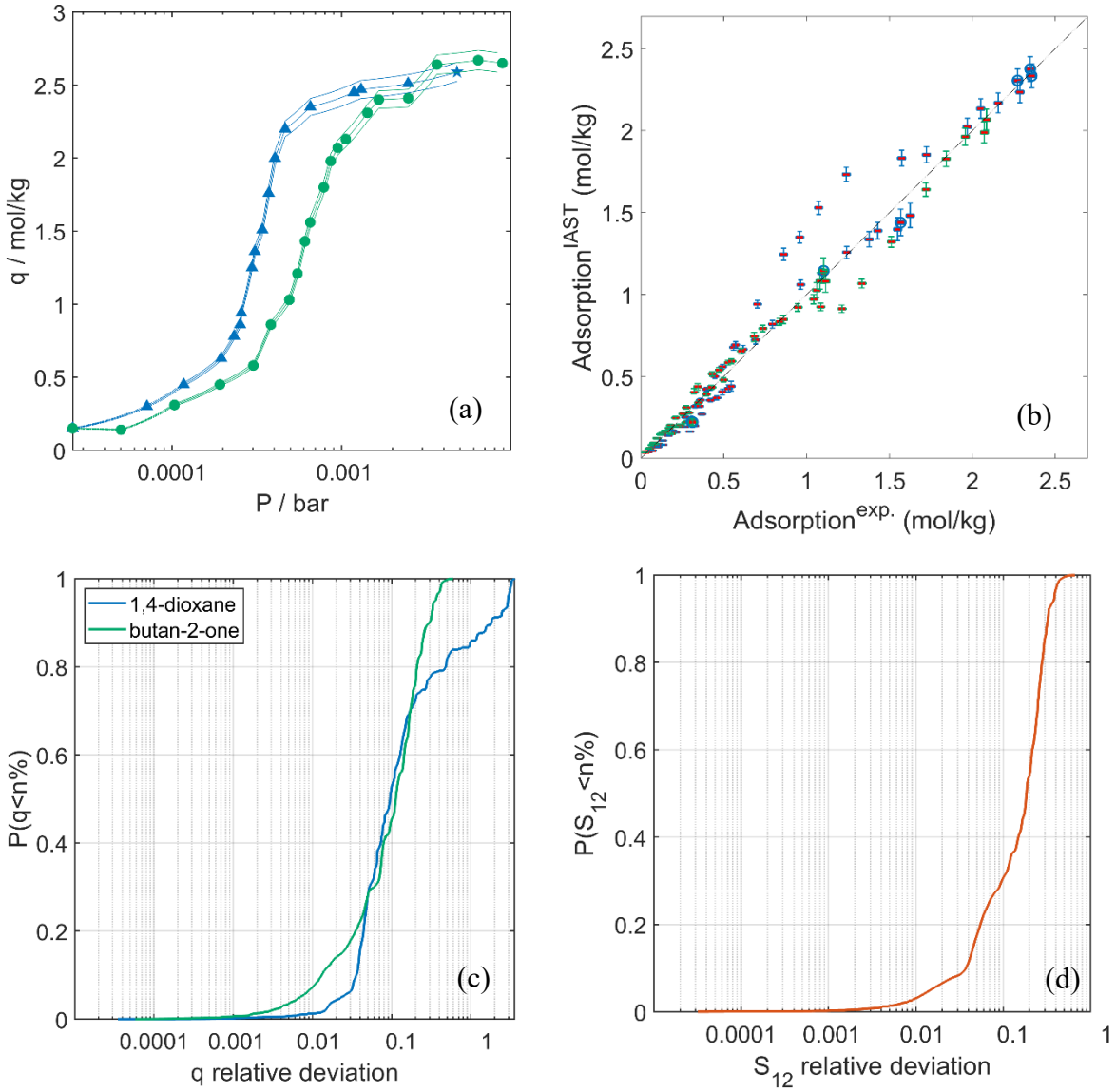



**Figure 1**: (a) The single-component isotherms of 1-dioxane (blue) and butan-2-one (green) in FAU Y zeolite at 298 K. The circles and triangles represent the experimental data and the solid lines represent the interpolated isotherms considering ±2.5% uncertainty. The single-component isotherm of 1-dioxane is linearly extrapolated up to 0.0048 bar (marked with a blue pentagon) in the IAST calculations. (b) A comparison between the distribution of mixture adsorption loadings of 1-dioxane (blue) and butan-2-one (green) in FAU Y zeolite at 298 K predicted by IAST and their corresponding experimental values. Boxes are drawn from the first quartile to the third quartile and the whiskers go from each quartile to the minimum or maximum of the distribution

of IAST predictions. The horizontal line shows the median of the IAST predictions. Blue circles represent IAST predictions made using extrapolated 1,4-dioxane single-component data. (c) A cumulative plot of the relative deviation of the IAST predictions for the loading of each component compared with the corresponding experimental values. (d) A cumulative plot of the relative deviation for selectivity predicted by IAST and the corresponding experimental data.

A second example of our calculations is shown in Figure 2 for adsorption of prop-1-ene and propane in Activated Carbon Black Pearls I at 298.15 K.[28] Applying IAST requires extrapolation of the single-component data beyond 0.392 bar for prop-1-ene and 0.91 bar for propane. We used this data to test two different methods for extrapolating the single-component data. The default approach in the pyIAST package is to treat the loading reported at the highest pressure as the saturation loading. This choice defines a fixed loading beyond the highest pressure as shown in Figure 2(a). As a second approach, we fitted a line to the two state points with the highest pressures and extrapolated the single-component data beyond the highest pressure using that line (see Figure 2(c)). The interpolated and extrapolated curves in Figure 2(c) show curvature because of the logarithmic axis used for pressure in the figure. Neither of these extrapolation approaches is appropriate for all possible situations, but they have the virtue of simplicity. More information about these calculations and sample code is available in the Supporting Information.

IAST predictions made by the two extrapolated sets of isotherms shown in Figures 1(b) and 1(d). As might be expected from a visual comparison of the extrapolated isotherms, IAST is considerably more accurate when the linear extrapolation is used instead of the assumption of saturation loading. More specifically, the IAST selectivity predictions have a relative error <20% in 42% of the cases in Figure 2(b) and in 88% of the cases in Figure 2(d). Based on this and several similar comparisons (data not shown) we opted to use the linear extrapolation approach in all calculations reported below. Further improvements could be made in specific examples by fitting appropriate continuous functions to the full range of single-component data but we have not attempted this. For a small number of isotherms, the linear extrapolation approach gave a negative slope as a function of increasing pressure, an unphysical result that is presumably associated with uncertainty in the experimental data. In these cases, extrapolation beyond the highest reported pressure was performed using a line of best fit fitted to the highest six pressure values.

The challenges associated with extrapolation of single component isotherms in IAST are particularly pronounced in examples with high adsorption selectivity. In these cases the less favored species is weakly adsorbed and application of IAST often requires integration of this component's isotherm to unphysically high pressures[29]. Methods to systematically overcome this issue when using molecular simulation data exist [9], but when using experimental data there is no option other than choosing a well-defined approach to extrapolating the available single component data.

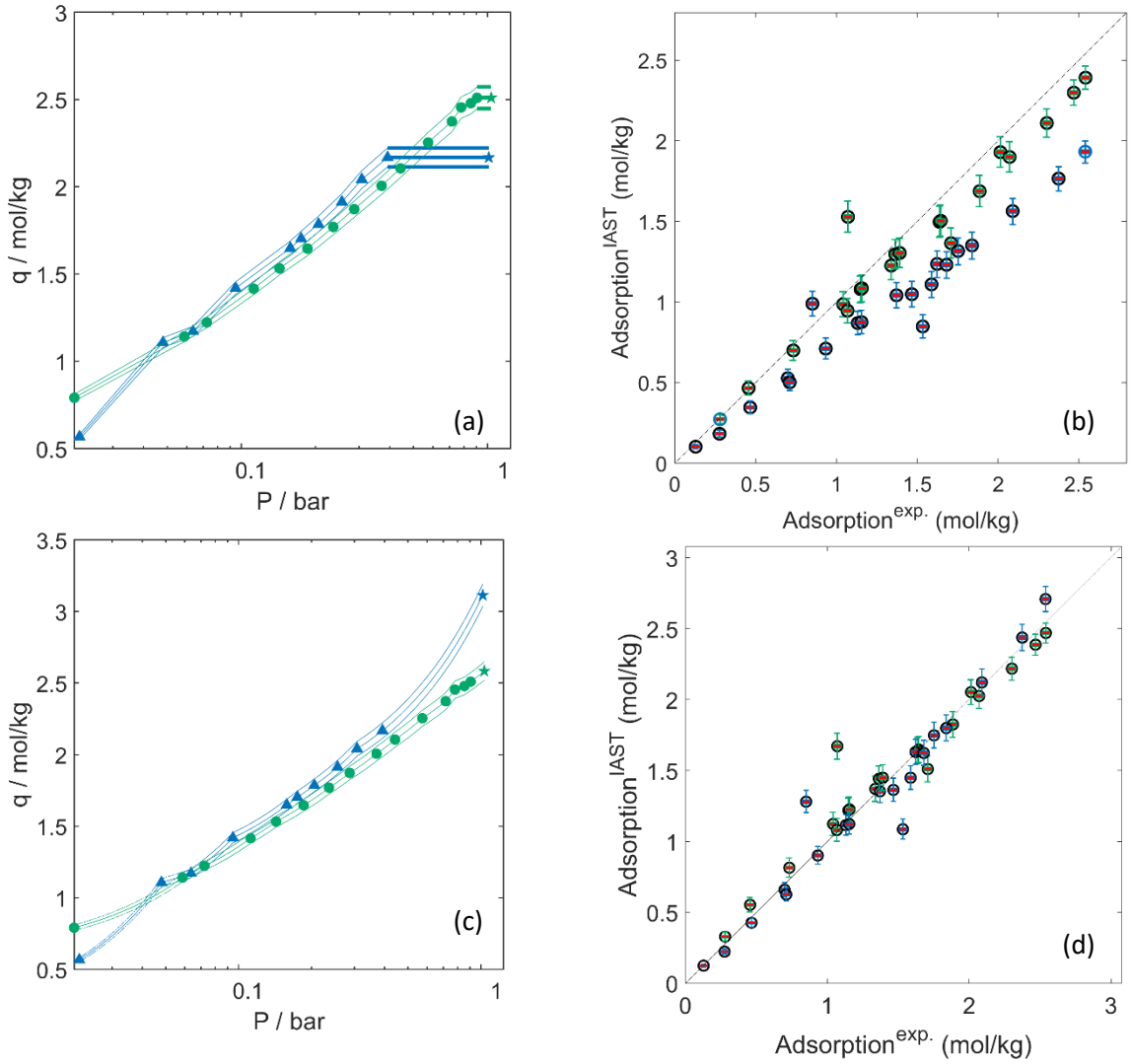


**Figure 2:** (a) and (c) Single-component isotherms of prop-1-ene (blue) and propane (green) in Activated Carbon Black Pearls I at 298.15 K. The circles and triangles represent the experimental data and the thin solid lines represent the interpolated isotherms considering ±2.5% uncertainty. The thick solid lines represent the extrapolated isotherms needed for IAST defined as described in the text. (b) and (d) The distribution of mixture adsorption loadings of prop-1-ene (blue) and propane (green) in Activated Carbon Black Pearls I at 298.15 K predicted by IAST using the single-component data extrapolated as shown in (a) and (c), respectively, and their corresponding experimental values. Black circles represent IAST predictions that required extrapolated prop-1-ene and propane single-component data.

Having illustrated our methods with these two examples, we now turn to applying IAST to the full collection of data described above. Instead of directly comparing loadings of adsorbed components with their corresponding experimental values, we used adsorption selectivity as the main measure of the precision of IAST in describing mixture adsorption. To this end, we calculated the probability of predicting selectivity by IAST with relative deviations of <5, <10, <20, <50, and <100% (see Table S6 for $P(S_{12} < n\%)$ where n is 5, 10, 20, 50, and 100). The level of relative deviation that might be considered acceptable is likely to differ depending on the specific application being studied and the maturity of separations processes for that application. We applied the methods illustrated above to each of the 411 collections of binary adsorption data obtained from the BISON data set. This analysis included 6,887 independent binary adsorption data points from experimental data and 833,327 IAST calculations making predictions for these data points.

Figure 3(a) shows the number of examples among these 411 examples as a function of the probability of predicting $S_{12}$ with a relative deviation <5, <10, <20, <50, or <100% for the complete set of state points in an example. As indicated in Figure 3(a), IAST makes 80% of $S_{12}$ predictions with a relative deviation <5, <10, <20, <50, and <100% in 4, 37, 86, 211, and 331 of the 411 total examples. In 325 of the examples, at least one of the state points required the use of extrapolated single-component data to make an IAST prediction. Figure 3(b) shows the outcomes from the complete collection of state points for each of these 325 examples with solid lines. The equivalent results obtained from only considering the state points that required extrapolated data are shown in Figure 3(b) with dotted lines. As in the specific example given above, IAST predictions made

using extrapolated single-component data are generally less accurate than the rest of the IAST predictions, although the difference between the two situations is not dramatic.

The data shown in Figure 3 weights each reported binary adsorption isotherm from the BISON dataset equally, and the analysis of each isotherm weighted each individual state point equally. It is interesting to perform a similar analysis for the subsets of isotherms available for particular gas mixtures. Information of this kind is shown in Figure 4 for the 10 most common gas mixtures among the 411 examples from the BISON data set. By the metric used here, the subset of examples for $CO_2/CH_4$ mixtures has a similar level of accuracy with IAST to the full collection of examples, while $C_2H_6/C_2H_4$ and $N_2/CH_4$ have higher levels of accuracy and $CO_2/N_2$ have lower levels of accuracy.

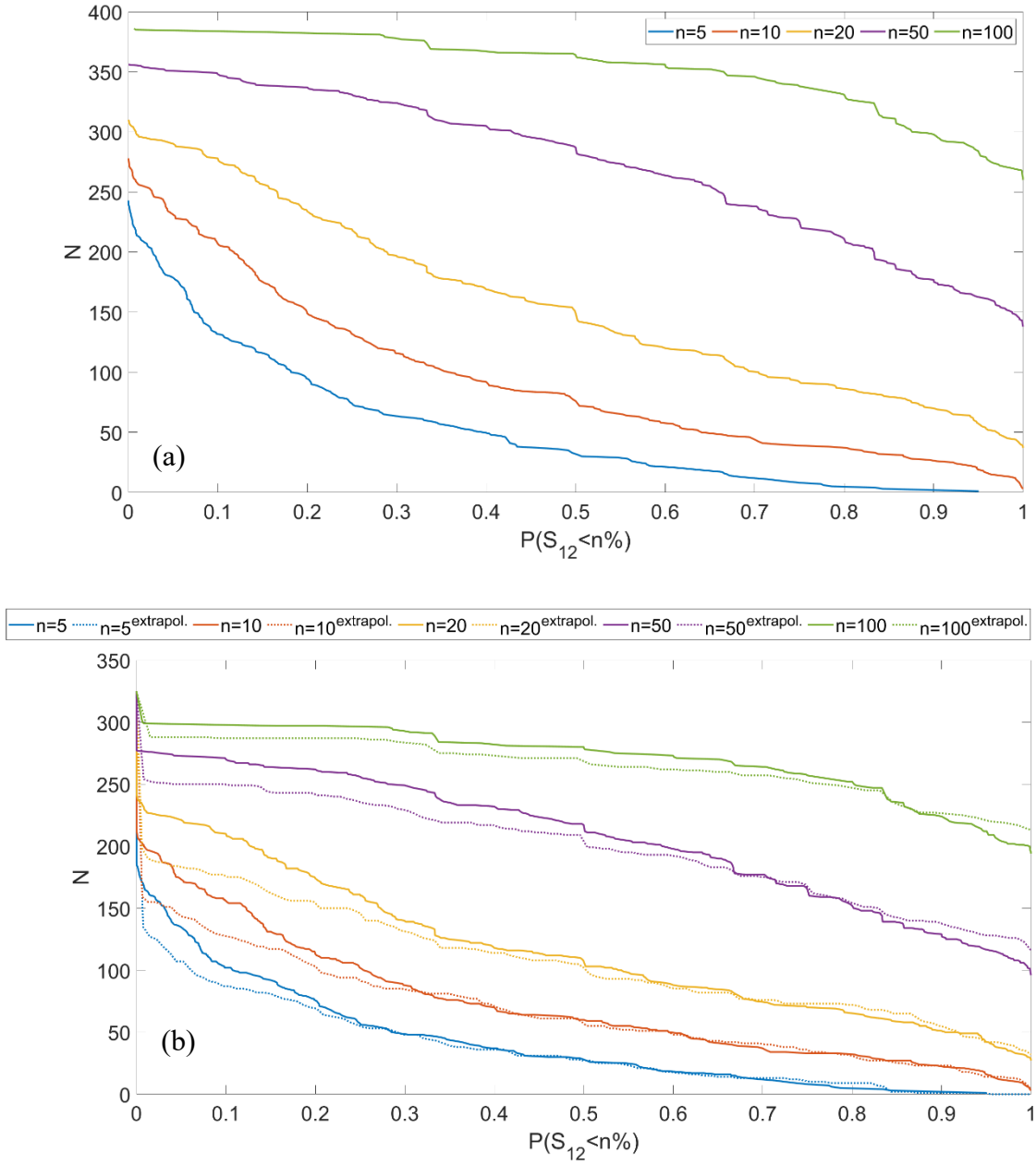



**Figure 3**: (a) The relationship between the number of binary adsorption systems from the BISON dataset and the probability of predicting $S_{12}$ by IAST with a relative deviation <5%, <10%, <20%, <50%, and <100% compared with the experimental data. (b) Similar to (a), but comparing results from the 325 binary adsorption systems in which least one of the state points required the use of extrapolated single-component data (solid lines) and the predictions from these 325 examples

considering only the state points where application of IAST required extrapolated single-component data (dashed lines).

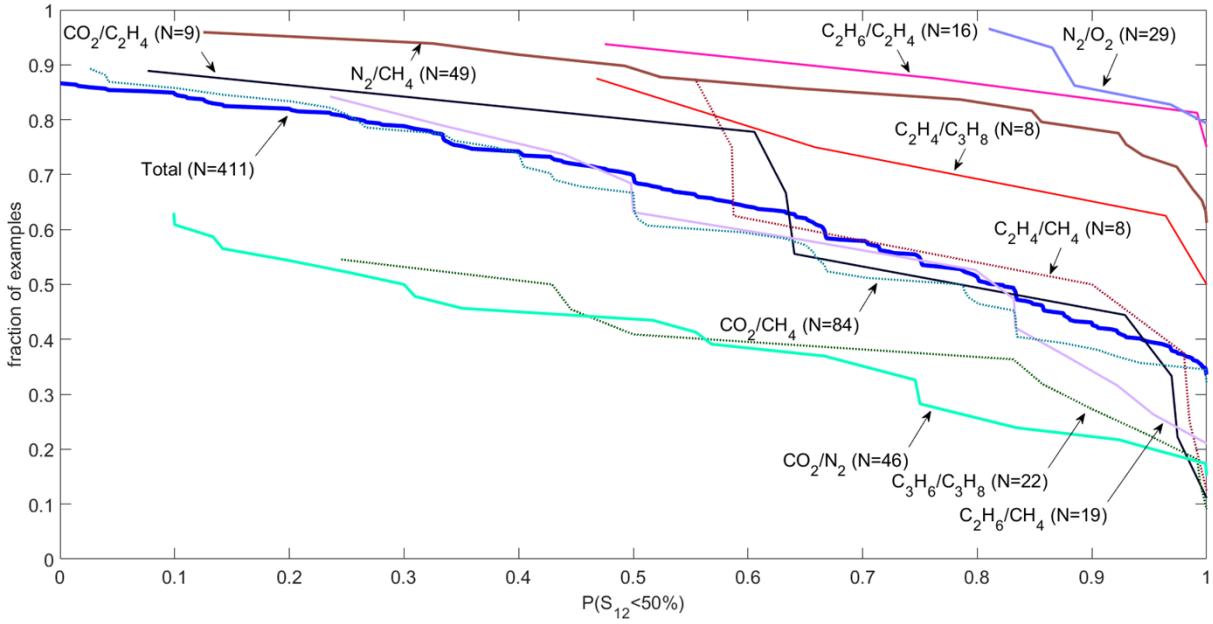



**Figure 4:** The fraction of examples as a function of the probability of predicting $S_{12}$ by IAST with a relative deviation <50% based on the complete set of 411 examples and for the examples comprising the 10 most-studied gas mixtures.

## Carbon dioxide/Methane gas mixtures

~20% (84 of 411) of all binary adsorption examples from the BISON-20 data set we were able to analyze with IAST are $CO_2/CH_4$ binary mixtures. In 24 of these 84 examples, every state point requires the use of extrapolation to make IAST predictions. Figure 5 shows the relationship between the number of examples based on the 84 $CO_2/CH_4$ examples and the probability of predicting $S_{12}$ with a relative deviation <5, <10, <20, <50, and <100%, respectively. IAST makes 80% of the $S_{12}$ predictions with a relative deviation <5, <10, <20, <50, and <100% in 2, 7, 17, 39,

and 63 examples, respectively. The trends for $CO_2/CH_4$ are similar to those for the complete collection of examples from the BISON-20 data set (see Figure 4).

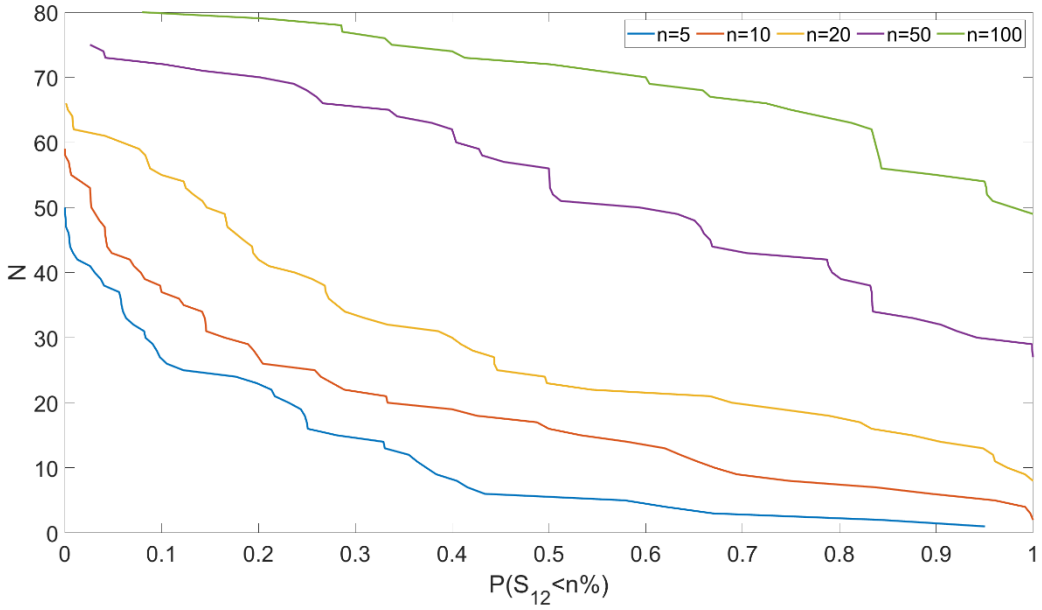



**Figure 5:** The relationship between the number of $CO_2/CH_4$ binary adsorption systems from the BISON-20 data set and the probability of predicting $S_{12}$ by IAST with a relative deviation <5, <10, <20, <50, and <100% compared with the experimental data.

We do not observe any obvious relationship between the type of the sorbents and the quality of their $S_{12}$ predictions for $CO_2/CH_4$ mixtures. IAST predicts $S_{12}$ for 100% of the available state points with a relative deviation <50% for a range of sorbents, including activated carbons[30-40], zeolites[41-43], metal-organic frameworks[44-46], and functionalized polymers[47]. There are, however, materials for which IAST makes no $S_{12}$ prediction with a relative deviation <50%, such as the porous organic polymer with structure codes DATPIM [47] and a carbon xerogel[48], zeolite NaX[49], and the MOFs amino-MIL53(Al)[50] and SION-8P[51].

It is interesting to explore the trends in the precision of IAST as a function of gas phase pressure, composition and temperature. In general, it might be expected that IAST would become

more accurate as pressure is lowered and as temperature is increased, since bulk mixtures become more ideal under these circumstances. A similar analysis to the one presented below for $CO_2/CH_4$ mixtures is presented for all the 411 binary systems in the Supporting Information.

Figure 6(a) shows cumulative plots of the relative deviation of the $S_{12}$ predictions made by IAST for $CO_2/CH_4$ binary adsorption for different ranges of total pressure. To reduce effects associated with the experimental challenges of accurately measuring mixtures in which one component is dilute[19], Figure 6(b) replots the data from Figure 6(a) after excluding examples where the gas phase composition is dilute for one component, specifically, $y_{CO_2} < 0.1$ or $y_{CO_2} > 0.9$). There is a marked decrease in the accuracy of the IAST predictions for total pressures >10 bar compared to results from lower pressures.

Figure 6(c) shows cumulative plots of the relative deviation of the $S_{12}$ predictions made by IAST for $CO_2/CH_4$ binary adsorption for different ranges of temperature. There is no obvious physical trend in these results. The accuracy of IAST predictions at temperatures close to room temperature are noticeably higher than higher and lower temperatures. The results with 318 < T < 328 K show considerably lower accuracy than every other temperature range, both higher and lower temperatures. We speculate that these trends are associated with details of experimental methods and data rather than from any underlying physical trend.

Figure 6(d) shows cumulative plots of the relative deviation of the $S_{12}$ predictions made by IAST for $CO_2/CH_4$ binary adsorption for different ranges of the $CO_2$ gas-phase mole fractions. The quality of IAST predictions when one of the gas phase components is dilute ($y_{CO_2} < 0.1$ or $y_{CO_2} > 0.9$ ) is much lower than the rest of the predictions, consistent with previous reports[19]. This situation is likely to arise primarily from challenges in making precise experimental measurements in this regime rather than any physical trend associated with IAST.

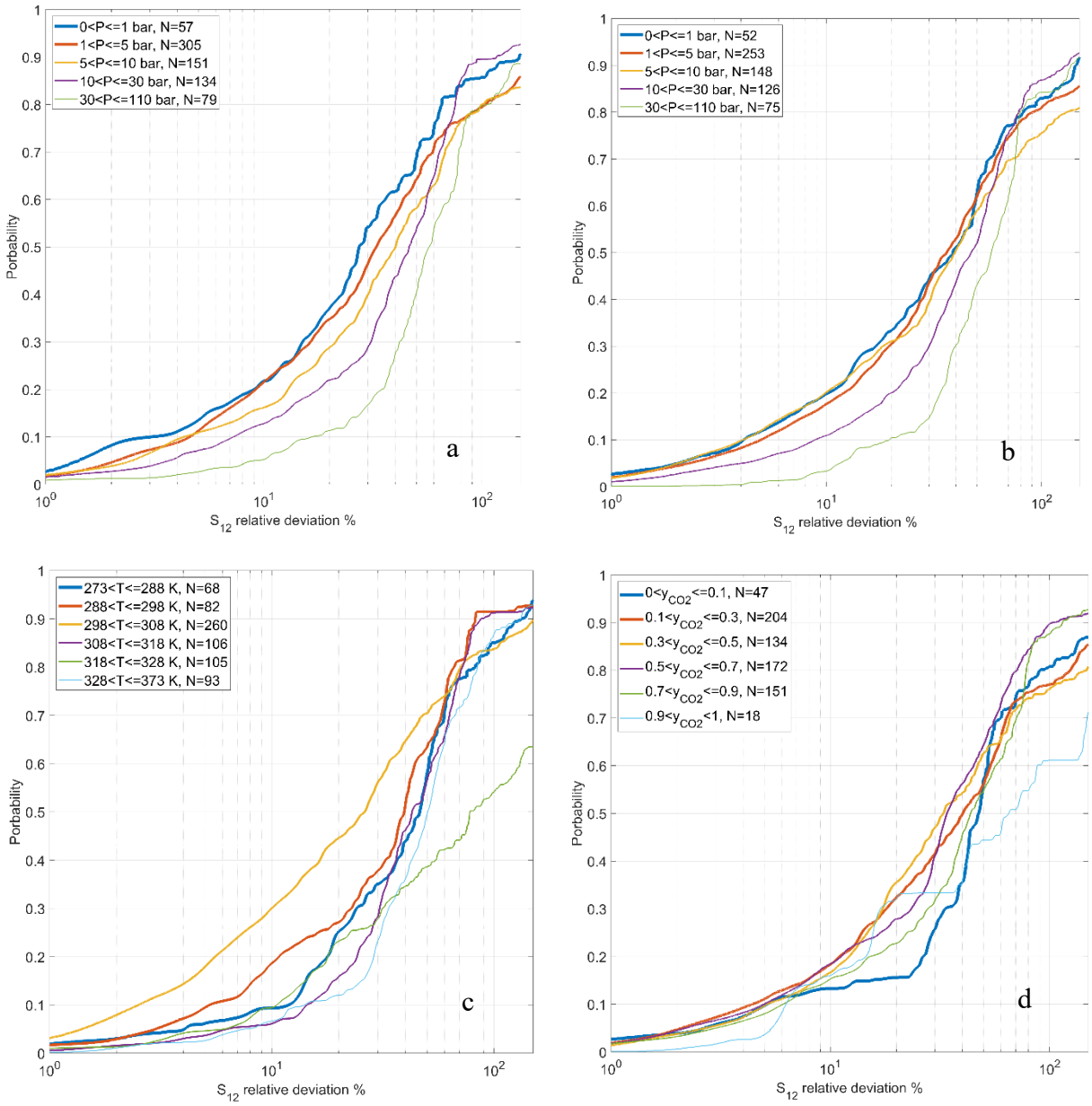



Figure 6- (a) Cumulative plots of the relative deviation of the $S_{12}$ predictions made by IAST for $CO_2/CH_4$ binary adsorption systems based on different ranges of total adsorption pressures. (b) Similar to (a) but excluding the state points reported at low gas-phase mole fraction of the components ($y_{CO_2} < 0.1$ or $y_{CO_2} > 0.9$). (c) Cumulative plots of the relative deviation of the $S_{12}$ predictions made by IAST for $CO_2/CH_4$ binary adsorption systems based on different ranges of temperatures. (d) Cumulative plots of the relative deviation of the $S_{12}$ predictions made by IAST for $CO_2/CH_4$ binary adsorption systems based on different ranges of $CO_2$ gas-phase mole fractions.

**Nitrogen/Methane gas mixtures**

12% of the binary adsorption examples we examined (49 of 411) are $N_2/CH_4$ binary gas mixtures. As indicated in Table S6, IAST makes 100% of $S_{12}$ predictions with a relative deviation <5, <10, <20, <50, and <100% in 0 (0%), 1 (2%), 13 (26.5%), 30 (61.2%), and 40 (81.6%) examples, respectively. There are no $S_{12}$ prediction with a relative deviation <5, <10, <20, <50, and <100% in 12, 7, 5, 2, and 0 examples. Figure 7 shows a relationship between the number of examples based on the 49 $N_2/CH_4$ examples and the probability of predicting $S_{12}$ with a relative deviation <5, <10, <20, <50, and <100%, respectively. As indicated in Figure 7, IAST makes 80% of $S_{12}$ predictions with a relative deviation <5, <10, <20, <50, and <100% in 2, 7, 17, 39, and 63 examples, respectively.

IAST makes 100% of the $S_{12}$ predictions we examined using extrapolated single-component data for 16 examples. As indicated in Figure 4, the accuracy of IAST in $N_2/CH_4$ examples is higher than for the overall range of mixtures we analyzed. Two examples for which IAST was found to be particularly inaccurate for $N_2/CH_4$ mixtures were $Ni_3(HCOO)_6$ [52] and $H^+$-mordenite[53].

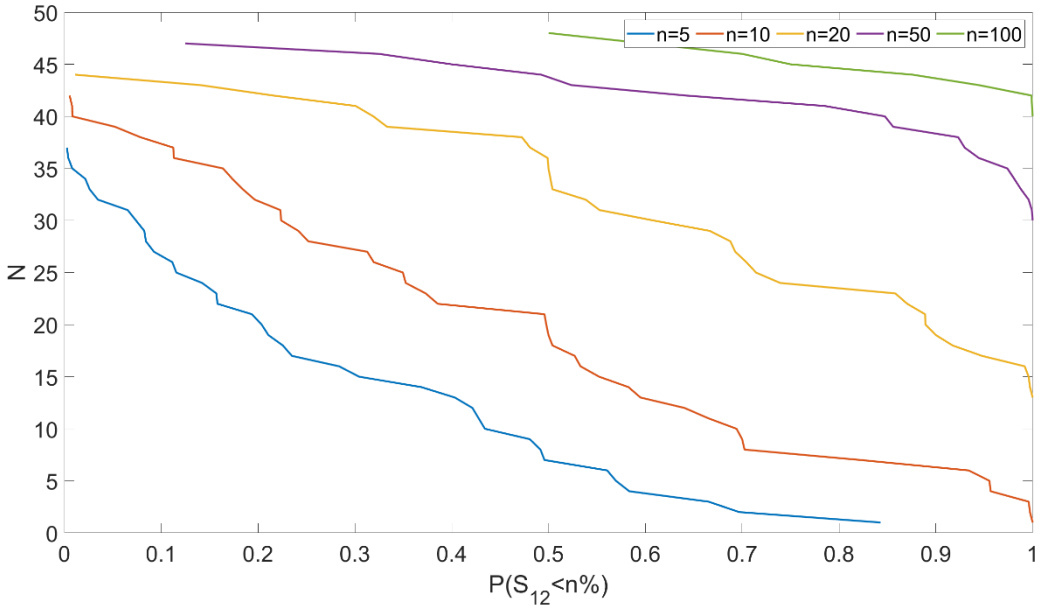


**Figure 7-** The relationship between the number of $N_2/CH_4$ examples and the probability of predicting $S_{12}$ by IAST with a relative deviation <5, <10, <20, <50, and <100% compared with the experimental data.

**Carbon dioxide/Nitrogen gas mixtures**

11% of the total binary adsorption examples we analyzed were $CO_2/N_2$ mixtures (46 out of 411). As indicated in Table S6, IAST makes 100% of $S_{12}$ predictions with a relative deviation <5, <10, <20, <50, and <100% in 0 (0%), 0 (0%), 3 (6.5%), 7 (15.2%), and 27 (58.7%) examples, respectively, and no $S_{12}$ predictions with a relative deviation <5, <10, <20, <50, and <100% in 33, 30, 24, 17, and 8 cases. Figure 8 shows a relationship between the number of examples based on the 46 $CO_2/N_2$ examples and the probability of predicting their $S_{12}$ with different relative deviations. IAST makes 80% of $S_{12}$ predictions with a relative deviation <5, <10, <20, <50, and <100% in 0, 3, 4, 11, and 33 examples, respectively.

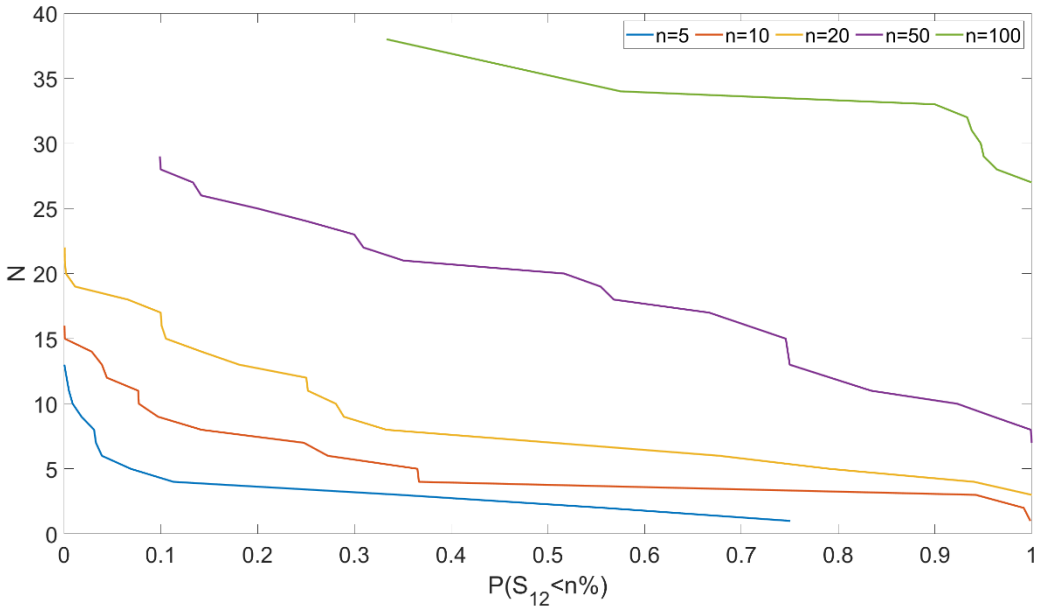



**Figure 8** The relationship between the number of $CO_2/N_2$ examples and the probability of predicting $S_{12}$ by IAST with a relative deviation <5, <10, <20, <50, and <100% compared with experimental data.

100% of the $S_{12}$ predictions for $CO_2/N_2$ mixtures with IAST required extrapolated single-component data in 33 of the 49 examples. As indicated in Figure 4, the IAST success rate in describing $CO_2/N_2$ examples is one of the lowest among the 10 most-studied binary gas mixtures examples. It may be that the large number of cases that relied on extrapolation of the single-component isotherms is a key contributor to this situation. We could not observe any obvious relationship between the type of sorbents and the quality of $S_{12}$ predictions made by IAST for $CO_2/N_2$. Materials for which IAST makes 100% of $S_{12}$ predictions with a relative deviation <50% included multiple activated carbons [32, 38, 40, 54] and the metal-organic framework MOF-508b[44].

**Nitrogen/Oxygen gas mixtures**

7% of the binary adsorption examples are $N_2/O_2$ binary gas mixtures (29 out of 411). As indicated in Table S6, IAST makes 100% of $S_{12}$ predictions with a relative deviation <5, <10, <20, <50, and <100% in 0 (0%), 0 (0%), 5 (17.2%), 23 (79.3%), and 28 (96.5%) examples, respectively, and no $S_{12}$ prediction with a relative deviation <5, <10, <20, <50, and <100% in 4, 2, 1, 1, and 1 case. Figure 9 shows a relationship between the number of examples based on the 29 $N_2/O_2$ examples and the probability of predicting their $S_{12}$ with various relative deviations <5, <10, <20, <50. IAST makes 80% of $S_{12}$ predictions with a relative deviation <5, <10, <20, <50, and <100% in 0, 14, 21, 28, and 28 examples, respectively. As indicated in Figure 4, the success rate of IAST in describing $N_2/O_2$ is on average higher than the other nine most-studied binary gas mixtures.

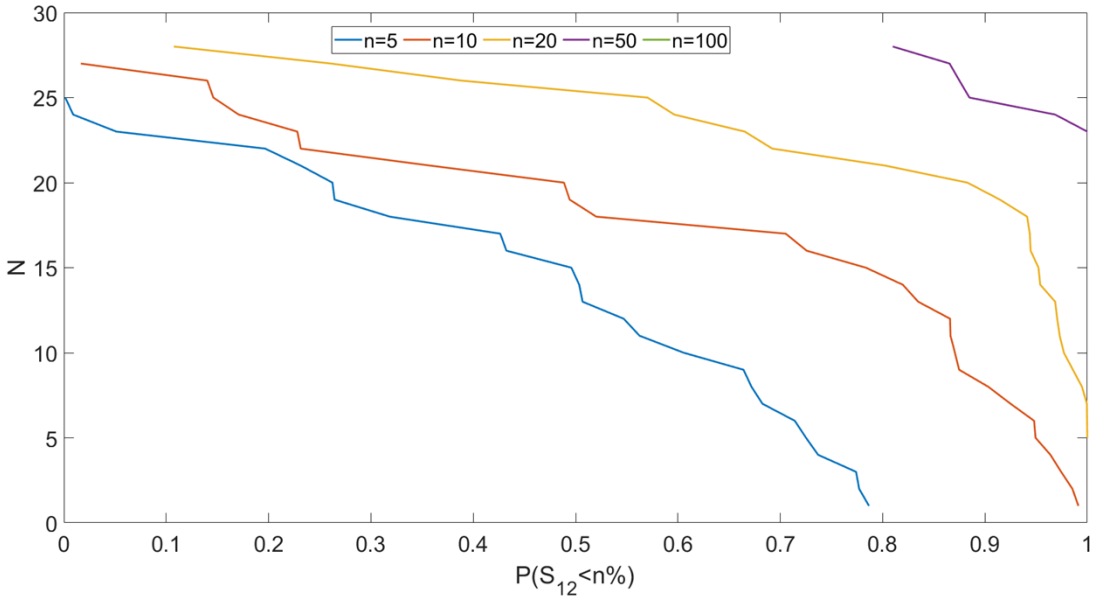



**Figure 9-** The relationship between the number of $N_2/O_2$ examples and the probability of predicting $S_{12}$ by IAST with a relative deviation <5, <10, <20, <50, and <100% compared with experimental data.

**Prop-1-ene/Propane gas mixtures**

5.6% of the binary adsorption examples are $C_3H_6/C_3H_8$ gas mixtures (22 out of 411). As indicated in Table S6, IAST makes 100% of the $S_{12}$ predictions with a relative deviation <5, <10, <20, <50, and <100% in 0 (0%), 0 (0%), 0 (0%), 2 (9.1%), and 7 (31.8%) examples, respectively, and no $S_{12}$ prediction with a relative deviation <5, <10, <20, <50, and <100% in 15, 14, 11, 10, and 6 cases. Figure 10 summarizes the predictions of IAST for $S_{12}$ for $C_3H_6/C_3H_8$ gas mixtures. IAST makes 80% of $S_{12}$ predictions with a relative deviation <5, <10, <20, <50, and <100% in 0, 0, 2, 8, and 9 examples, respectively. 100% of the IAST predictions used the extrapolated single-component data in 13 examples. As indicated in Figure 4, the IAST success rate in describing $C_3H_6/C_3H_8$ examples is one of the lowest among the 10 most-studied binary gas mixtures.

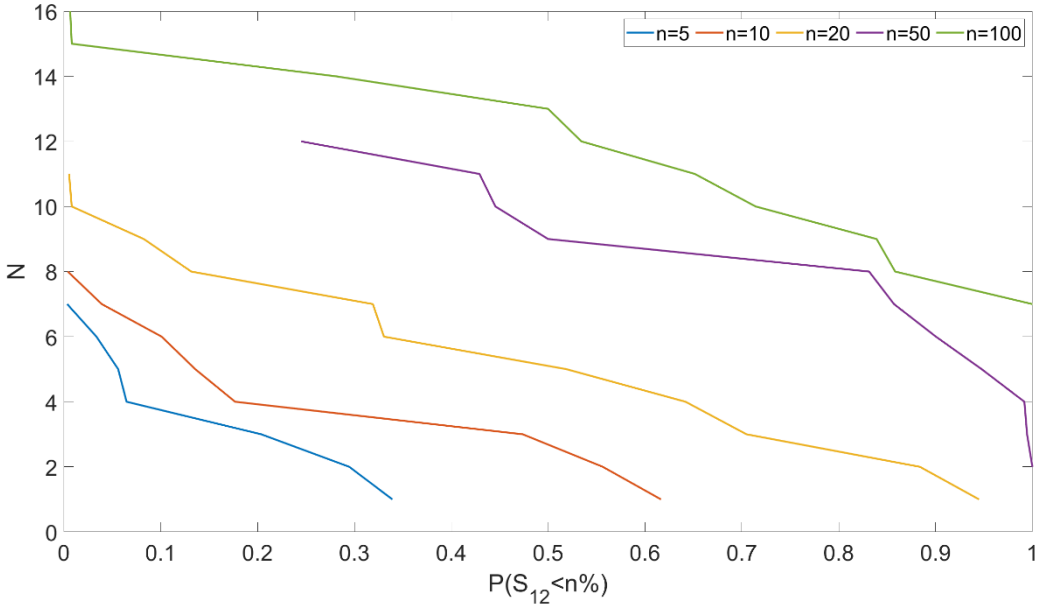



**Figure 10-** The relationship between the number of $C_3H_6/C_3H_8$ examples and the probability of predicting their $S_{12}$ by IAST with a relative deviation <5, <10, <20, <50, and <100% compared with the experimental data.

## Other gas mixtures

Each other gas mixture in our analysis comprises less than 5% of the complete collection of the 411 binary adsorption examples. This includes $C_2H_6/C_2H_4$ (3.9%), $CO_2/C_2H_4$ (2.2%), $C_2H_4/CH_4$ (1.9%), and $C_2H_4/C_3H_8$ (1.9%). Some highlights for each of these four mixtures are listed in the Supporting Information.

## Conclusion

We have presented a systematic comparison between experimental measurements of binary gas adsorption in porous adsorbents and predictions based on IAST, with data from over 400 distinct mixed gas isotherms. This collection is by far the most comprehensive comparison of this type that has been made, and it was enabled by the BISON-20 data set[16], a collection of over 900 mixed gas isotherms assembled from a systematic literature review. Because establishing consistency between experimental measurements taken by different groups with different material

samples is nontrivial[12, 55, 56], we only analyzed examples in which single-component and mixture experimental data was available from the same publication. We also assessed the role of experimental uncertainty for both single-component and mixture data by comparing ensembles of fitted single-component isotherms within our IAST calculations. Our analysis included 6,887 independent binary adsorption data points from experimental data and more than 833,000 IAST calculations making predictions for these data points. In addition to these IAST calculations we reported a number of corrections and updates to the BISON-20 data set that we recommend to future users of that data.

The accuracy that is required for a prediction of mixture adsorption to be considered "useful" will be dependent on the context in which such a prediction is to be used. We focused on predictions of adsorption selectivity, since this is a more challenging property to predict accurately than adsorbed loadings and it is often a key variable in selecting an adsorbent for a desired separation. In 9% of the isotherms we considered (37 of 411) the predictions of IAST for selectivity were within 10% of the experimental value for 80% or more of the available state points. In 51% of the isotherms (211 of 411), however, 80% or more of the available state points had predictions for selectivity within 50% of the experimental outcome. The level of agreement between IAST predictions and experiment typically decreased when experimental data associated with dilute gas phase mixtures or situations where extrapolation of fitted single-component isotherms beyond the range of experimental data was required for application of IAST. These two points are salient reminders that inaccuracy in IAST predictions can result from the underlying precision and range of the single-component data that is used and that caution should therefore be used in concluding that the fundamental assumptions of IAST are violated in examples of this kind. Our results provide examples illustrating that simply considering a mixture of molecules that are not chemically similar does not automatically mean that IAST gives poor predictions, as in the example of 1-dioxane/butan-2-one in FAU Y zeolite shown in Figure 1. We used a relatively simple approach to extrapolation that could readily be applied to the large number of examples we considered. Approaches that fit a physically motivated isotherm to the available data may further improve the performance of IAST in cases where extrapolation of one or both of the single component isotherms is necessary.

The large number of examples we analyzed made it possible to systematically consider the impact of temperature, pressure and gas phase composition on the accuracy of IAST. As has been noted previously, experimental measurements that involve dilute gas or adsorbed phase mixtures are especially prone to measurement uncertainty[19]. IAST is typically in poorer agreement with experiment for these situations than for other mixture compositions, but this seems most likely to be mainly due to experimental uncertainties. As might be expected, IAST was in general found to be more accurate at lower total pressures. The trends observed with temperature were less clear, with generally better agreement with experimental data for experiments near room temperature rather than either higher or lower temperatures. This observation suggests that experimental uncertainty at non-ambient conditions may be more substantial in reported data than in results from ambient temperatures.

We have studied IAST in this paper because it is the most widely used mixing theory for adsorption. There are of course a range of other mixing theories that aim to improve upon IAST. The large collection of experimental data and the treatment of experimental uncertainties we have reported here should be useful in future efforts to refine these mixing theories. Future tests of alternate mixing theories should, like the work here, use the entire data collection systematically since this is much more informative than focusing on a small subset of the data. This situation also highlights the need for alternate mixing theories to be readily automated for use with many examples, a prerequisite if they are to be used in most practical situations.

The data we have collated in this paper is also likely to be useful in applying tools from machine learning to task of predicting mixture adsorption and designing adsorption-based processes for chemical separations. Existing applications of machine learning to this task have almost exclusively been trained on adsorption data from molecular simulations[57-61] and extensions of this work to adsorbed mixtures has relied on IAST[10, 11]. Successes have been reported in creating machine learning models trained on experimental data for predicting the water stability of some classes of porous materials[62] and for the permeation of gases through polymeric membranes[63]. In these and other applications of machine learning, availability of a diverse data set for model training is a prerequisite. Our use in this paper of the BISON-20 data set is a demonstration of the large variety of mixture adsorption experiments that have been reported in the literature and the value of curating data sets of this kind.

## Supporting information

More details of the methods and results (pdf), initial binary adsorption data sets extracted from Bison 20, experimental data units, 424 binary mixture adsorption data sets, unique binary gas mixtures, systems excluded from 424 binary mixture adsorption data sets, details of the IAST calculations, updated Bison 20 single-component adsorption database, updated Bison 20 binary mixture adsorption database, uncertain single-component adsorption data used in IAST calculations, IAST calculation results, and sample pyIAST programs for IAST calculations (zip).

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The authors declare no competing financial interest.

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